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Structure of Tetrakis(μ-1,3-benzothiazole-2-thiolato-*N*,*S*)-diplatinum(II) Dimethylformamide Solvate

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Abstract. $[Pt_2(C_7H_4NS_2)_4].C_3H_7NO$, $M_r = 1128{\cdot}2$, triclinic, $P\bar{1}$, $a = 10{\cdot}301$ (1), $b = 12{\cdot}031$ (2), $c = 15{\cdot}090$ (2) Å, $\alpha = 76{\cdot}735$ (7), $\beta = 73{\cdot}340$ (6), $\gamma = 77{\cdot}293$ (5)°, $V = 1719{\cdot}8$ Å^3, $Z = 2$, $D_m = 2{\cdot}15$ (1), $D_x = 2{\cdot}178$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 8{\cdot}71$ mm^{-1}, $F(000) = 1072$, $T = 295$ K, $R = 0{\cdot}0265$ for 4824 observed reflections. Each of the two crystallographically independent centrosymmetric neutral dimers contains two square-planar Pt atoms [Pt—Pt = 2·761 (1) or 2·753 (1) Å] with *cis*-S_2N_2 coordination from four bridging 1,3-benzothiazole-2-thiolato ligands. Mean Pt—S and Pt—N distances are 2·284 and 2·076 Å, respectively. Ligand donor sites are exocyclic S and heterocyclic N atoms. The dimethylformamide molecules are not coordinated to the Pt atoms, but are located in cavities in the crystal structure.

Introduction. Complexes of 1,3-benzothiazole-2-thione (bztztH) and its anion (bztzt$^-$) have been extensively reported and reviewed (Raper, 1985). The thione form of bztztH has been shown to be the dominant solid-state tautomer (Chesick & Donohue, 1971; Radha, 1985). It has been proposed, however, that in its reactions with heavy metals at low pH (*e.g.* Pd, Pt, Ru), the tautomeric balance shifts towards the thiol form of bztztH with subsequent heterocyclic N donation to the metal (Wilson & Merchant, 1967; Dehand & Jordanov, 1976).

Several structural investigations have shown bztzt to be a versatile ligand. Towards Zn^{II}, monodentate S and monodentate N coordination have been reported (McCleverty, Morrison, Spencer, Ashworth, Bailey, Johnson, Smith, Tabbiner & Taylor, 1980). Monodentate S donation also occurs with Hg^{II} (Bravo, Casas, Castano, Gayoso, Mascareñhas, Sanchez, Santos & Sordo, 1985) and Ru^{II} (Jeannin, Jeannin & Lavigne, 1976*b*). The ligand is μ-S,N bridging towards Ru^{I} (Jeannin, Jeannin & Lavigne, 1976*a*) and Pd^{II} (Kubiak, 1985). S,N chelation is reported in the Cd(bztzt)$_3^-$ anion (McCleverty, Gill, Kowalski, Bailey, Adams, Lumbard & Murphy, 1982). An interesting combination of μ_2-S and μ-N bridging is also reported for bztzt in the complexes $[Re(bztzt)(CO)_3]_2$ and $[HRu_3(bztzt)(CO)_9]$ (Jeannin, Jeannin & Lavigne, 1976*c*, 1978).

We have extended the range of structural investigation for bztzt to Pt^{II} with this report.

Experimental. Bright-yellow crystals from a dimethylformamide (DMF) solution of the reaction product obtained from a hot aqueous solution of K_2PtCl_4 (1 mmol) and a hot aqueous ethanol solution of bztztH (2 mmol); crystal dimensions 0·15 × 0·19 × 0·29 mm, D_m by flotation in CCl_4/CH_3I. Siemens AED-2 diffractometer. Unit-cell parameters from 32 centred reflections ($20 < 2\theta < 25$°). 9639 reflections measured ($3 < 2\theta < 50$°), index ranges: h −11→8, k −14→14, l −17→17. Intensity decay of approximately 3% on three standard reflections incorporated into data reduction, empirical absorption correction, transmission 0·204–0·247. 5560 unique reflections, 4828 reflections with $F > 4\sigma(F)$, $R_{\rm int} = 0{\cdot}0197$. Structure solved by heavy-atom method, refined by blocked-cascade least squares on F to a minimum of $\sum w\Delta^2$. Anisotropic thermal parameters for all non-H atoms; ligand aromatic H atoms located on external bisectors of ring angles, C—H = 0·96 Å, $U(H) = 1{\cdot}2U_{\rm eq}(C)$. Dimethyl-

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formamide H atoms were not included. Isotropic extinction parameter $x = 1{\cdot}8\,(2) \times 10^{-7}$ [$F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{1/4}$]. Scattering factors from *International Tables for X-ray Crystallography* (1974), 425 parameters, $R = 0{\cdot}0265$, $wR = 0{\cdot}0247$, $w^{-1} = \sigma^2(F)$, $\Delta/\sigma_{\max} = 0{\cdot}047$, mean $= 0{\cdot}008$. Largest peak in final difference synthesis $+1{\cdot}14$ e Å^{-3}, close to Pt atoms, largest hole $-0{\cdot}78$ e Å^{-3}, $S = 1{\cdot}57$. Programs: *SHELXTL* (Sheldrick, 1985).

Discussion. Atomic coordinates and $U_{\rm eq}$'s are given in Table 1, bond lengths and selected bond angles in Table 2.* The structure of the binuclear complex and the atomic numbering used for one molecule are shown in Fig. 1. The numbering of the second molecule, with ligands 3 and 4, follows an analogous scheme. Dimethylformamide atoms are numbered O(51) to C(55). With two centrosymmetric binuclear metal complexes in a triclinic cell the asymmetric unit comprises the two half complexes plus one dimethylformamide molecule.

The absence of the ν(NH) band, which occurs at 3060 cm^{-1} in bztztH, in the IR spectrum of the complex, clearly indicated the ligand to be present as the bztzt anion. Furthermore, the occurrence of ν(Pt—S) and ν(Pt—N) at 360 and 240 cm^{-1}, respectively, suggested S,N coordination of the ligand to the metal.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$)

$U_{\rm eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	*y*	*z*	$U_{\rm eq}$
Pt(1)	140 (1)	468 (1)	714 (1)	28 (1)
S(11)	−660 (2)	−1062 (1)	1785 (1)	39 (1)
S(12)	−1471 (2)	−3276 (1)	1821 (1)	45 (1)
N(1)	−833 (4)	−1867 (3)	258 (3)	34 (2)
C(11)	−951 (5)	−1976 (4)	1180 (4)	33 (2)
C(12)	−1143 (6)	−2818 (5)	21 (4)	38 (2)
C(13)	−1060 (7)	−2978 (5)	−869 (4)	49 (3)
C(14)	−1399 (7)	−3973 (5)	−988 (5)	59 (3)
C(15)	−1808 (7)	−4824 (6)	−202 (5)	59 (3)
C(16)	−1875 (7)	−4681 (5)	696 (5)	53 (3)
C(17)	−1542 (6)	−3672 (5)	798 (4)	40 (2)
S(21)	−2048 (1)	1477 (1)	878 (1)	41 (1)
S(22)	−4396 (1)	1769 (1)	60 (1)	43 (1)
N(2)	−2136 (4)	434 (3)	−559 (3)	32 (2)
C(21)	−2704 (5)	1128 (4)	83 (4)	34 (2)
C(22)	−3006 (6)	414 (4)	−1104 (4)	35 (2)
C(23)	−2701 (6)	−165 (5)	−1853 (4)	44 (3)
C(24)	−3700 (7)	−80 (6)	−2322 (4)	57 (3)
C(25)	−4974 (7)	587 (6)	−2063 (5)	59 (3)
C(26)	−5308 (7)	1178 (5)	−1334 (4)	50 (3)
C(27)	−4303 (6)	1102 (5)	−863 (4)	39 (2)
Pt(2)	967 (1)	4038 (1)	4809 (1)	29 (1)
S(31)	−334 (2)	3434 (1)	4072 (1)	47 (1)
S(32)	−2975 (2)	4305 (1)	3569 (1)	54 (1)
N(3)	−2138 (4)	5426 (4)	4500 (3)	37 (2)
C(31)	−1789 (6)	4481 (5)	4126 (4)	43 (3)
C(32)	−3375 (6)	6064 (5)	4349 (4)	40 (2)
C(33)	−3974 (6)	7125 (5)	4610 (4)	53 (3)
C(34)	−5207 (7)	7673 (6)	4370 (5)	69 (3)
C(35)	−5846 (7)	7146 (6)	3927 (5)	67 (3)
C(36)	−5242 (7)	6107 (6)	3662 (5)	63 (3)
C(37)	−3998 (6)	5580 (5)	3864 (4)	48 (3)
S(41)	5 (2)	2950 (1)	6199 (1)	42 (1)
S(42)	−2252 (2)	3309 (1)	7876 (1)	42 (1)
N(4)	−1793 (4)	4974 (4)	6468 (3)	33 (2)
C(41)	−1328 (5)	3878 (5)	6752 (3)	31 (2)
C(42)	−2905 (5)	5439 (4)	7145 (4)	33 (2)
C(43)	−3580 (6)	6572 (5)	7060 (4)	43 (2)
C(44)	−4698 (6)	6878 (5)	7776 (4)	50 (3)
C(45)	−5140 (6)	6071 (5)	8562 (4)	47 (3)
C(46)	−4445 (6)	4947 (5)	8671 (4)	45 (2)
C(47)	−3338 (6)	4646 (4)	7956 (4)	36 (2)
O(51)	3142 (8)	849 (6)	4528 (4)	132 (4)
C(52)	2146 (13)	511 (8)	5041 (7)	133 (6)
N(53)	2047 (8)	−185 (6)	5862 (5)	98 (4)
C(54)	3171 (14)	−625 (13)	6316 (8)	191 (9)
C(55)	715 (13)	−482 (12)	6401 (9)	175 (9)

Table 2. *Bond lengths* (Å) *and selected bond angles* (°)

Pt(1)—Pt(1$^{\rm i}$)	2·761 (1)	Pt(2)—Pt(2$^{\rm ii}$)	2·753 (1)
Pt(1)—S(11)	2·285 (2)	Pt(2)—S(31)	2·282 (2)
Pt(1)—S(21)	2·287 (2)	Pt(2)—S(41)	2·283 (2)
Pt(1)—N(1$^{\rm i}$)	2·070 (4)	Pt(2)—N(3$^{\rm ii}$)	2·081 (6)
Pt(1)—N(2$^{\rm i}$)	2·078 (4)	Pt(2)—N(4$^{\rm ii}$)	2·074 (4)
S(11)—C(11)	1·702 (7)	S(31)—C(31)	1·728 (6)
S(12)—C(11)	1·745 (5)	S(32)—C(31)	1·740 (8)
S(12)—C(17)	1·742 (7)	S(32)—C(37)	1·730 (6)
N(1)—C(11)	1·339 (7)	N(3)—C(31)	1·320 (8)
N(1)—C(12)	1·398 (8)	N(3)—C(32)	1·385 (7)
C(12)—C(13)	1·376 (10)	C(32)—C(33)	1·381 (9)
C(12)—C(17)	1·398 (7)	C(32)—C(37)	1·385 (11)
C(13)—C(14)	1·382 (11)	C(33)—C(34)	1·401 (10)
C(14)—C(15)	1·406 (9)	C(34)—C(35)	1·383 (13)
C(15)—C(16)	1·386 (11)	C(35)—C(36)	1·362 (10)
C(16)—C(17)	1·383 (10)	C(36)—C(37)	1·384 (10)
S(21)—C(21)	1·701 (7)	S(41)—C(41)	1·710 (5)
S(22)—C(21)	1·751 (6)	S(42)—C(41)	1·754 (5)
S(22)—C(27)	1·730 (7)	S(42)—C(47)	1·753 (5)
N(2)—C(21)	1·345 (7)	N(4)—C(41)	1·317 (6)
N(2)—C(22)	1·386 (8)	N(4)—C(42)	1·407 (6)
C(22)—C(23)	1·386 (9)	C(42)—C(43)	1·382 (7)
C(22)—C(27)	1·406 (7)	C(42)—C(47)	1·394 (7)
C(23)—C(24)	1·382 (11)	C(43)—C(44)	1·383 (8)
C(24)—C(25)	1·381 (9)	C(44)—C(45)	1·383 (8)
C(25)—C(26)	1·367 (10)	C(45)—C(46)	1·381 (8)
C(26)—C(27)	1·391 (10)	C(46)—C(47)	1·374 (7)
O(51)—C(52)	1·184 (13)	C(52)—N(53)	1·318 (11)
N(53)—C(54)	1·451 (17)	N(53)—C(55)	1·454 (15)

S(11)—Pt(1)—S(21)	90·4 (1)	S(31)—Pt(2)—S(41)	90·2 (1)
S(11)—Pt(1)—Pt(1$^{\rm i}$)	89·8 (1)	S(31)—Pt(2)—Pt(2$^{\rm ii}$)	92·7 (1)
S(21)—Pt(1)—Pt(1$^{\rm i}$)	90·5 (1)	S(41)—Pt(2)—Pt(2$^{\rm ii}$)	91·8 (1)
S(11)—Pt(1)—N(1$^{\rm i}$)	179·0 (1)	S(31)—Pt(2)—N(3$^{\rm ii}$)	179·1 (1)
S(21)—Pt(1)—N(1$^{\rm i}$)	88·6 (1)	S(41)—Pt(2)—N(3$^{\rm ii}$)	88·9 (1)
Pt(1$^{\rm i}$)—Pt(1)—N(1$^{\rm i}$)	90·0 (1)	Pt(2$^{\rm ii}$)—Pt(2)—N(3$^{\rm ii}$)	87·4 (1)
S(11)—Pt(1)—N(2$^{\rm i}$)	90·1 (1)	S(31)—Pt(2)—N(4$^{\rm ii}$)	88·3 (2)
S(21)—Pt(1)—N(2$^{\rm i}$)	179·5 (1)	S(41)—Pt(2)—N(4$^{\rm ii}$)	178·4 (2)
Pt(1$^{\rm i}$)—Pt(1)—N(2$^{\rm i}$)	89·6 (1)	Pt(2$^{\rm ii}$)—Pt(2)—N(4$^{\rm ii}$)	87·7 (1)
N(1$^{\rm i}$)—Pt(1)—N(2$^{\rm i}$)	90·9 (2)	N(3$^{\rm ii}$)—Pt(2)—N(4$^{\rm ii}$)	92·5 (2)
Pt(1)—S(11)—C(11)	107·6 (2)	Pt(2)—S(31)—C(31)	104·4 (3)
C(11)—S(12)—C(17)	90·7 (3)	C(31)—S(32)—C(37)	90·1 (3)
C(11)—N(1)—C(12)	113·2 (4)	C(31)—N(3)—C(32)	111·9 (6)
C(11)—N(1)—Pt(1$^{\rm i}$)	122·7 (4)	C(31)—N(3)—Pt(2$^{\rm ii}$)	125·2 (4)
C(12)—N(1)—Pt(1$^{\rm i}$)	124·0 (4)	C(32)—N(3)—Pt(2$^{\rm ii}$)	122·9 (4)
S(11)—C(11)—S(12)	117·5 (3)	S(31)—C(31)—S(32)	115·9 (4)
S(11)—C(11)—N(1)	129·9 (4)	S(31)—C(31)—N(3)	130·4 (6)
S(12)—C(11)—N(1)	112·6 (4)	S(32)—C(31)—N(3)	113·7 (4)
Pt(1)—S(21)—C(21)	106·7 (2)	Pt(2)—S(41)—C(41)	105·3 (2)
C(21)—S(22)—C(27)	90·8 (3)	C(41)—S(42)—C(47)	90·6 (2)
C(21)—N(2)—C(22)	113·0 (4)	C(41)—N(4)—C(42)	112·6 (4)
C(21)—N(2)—Pt(1$^{\rm i}$)	122·3 (4)	C(41)—N(4)—Pt(2$^{\rm ii}$)	125·0 (3)
C(22)—N(2)—Pt(1$^{\rm i}$)	124·7 (3)	C(42)—N(4)—Pt(2$^{\rm ii}$)	122·4 (3)
S(21)—C(21)—S(22)	116·7 (3)	S(41)—C(41)—S(42)	116·6 (3)
S(21)—C(21)—N(2)	130·9 (4)	S(41)—C(41)—N(4)	130·1 (4)
S(22)—C(21)—N(2)	112·4 (5)	S(42)—C(41)—N(4)	113·3 (4)
O(51)—C(52)—N(53)	127·5 (12)	C(52)—N(53)—C(54)	124·5 (10)
C(52)—N(53)—C(55)	119·3 (10)	C(54)—N(53)—C(55)	116·1 (8)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, 1-y, 1-z$.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of valence angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43952 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Structurally, the complex consists of pairs of Pt atoms bridged by four bztzt ligands with an inversion centre midway between the two metal atoms. The DMF molecules are not coordinated and consequently there are no additional axial contacts to Pt. These structural features are similar to those reported for the corresponding Pd^{II} complex (Kubiak, 1985). The DMF molecules are located in cavities in the crystal structure (Fig. 2).

Each Pt atom effectively has square-based pyramidal geometry. Pairs of thiolato S and hetero N atoms occupy the basal plane with the symmetry-related Pt atom in the apical position at a distance of 2·761 (1) or 2·753 (1) Å. The *cis*-PtS_2N_2 groups have an eclipsed configuration and are essentially square planar with angles at the Pt atom in the range 88·3–92·5°. The Pt atoms are displaced from the coordination planes by 0·0012 [Pt(1)] and 0·0056 Å [Pt(2)].

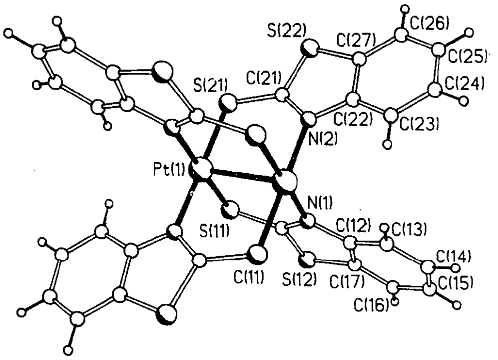

Fig. 1. Structure of one dimeric molecule, with the atom-numbering scheme.

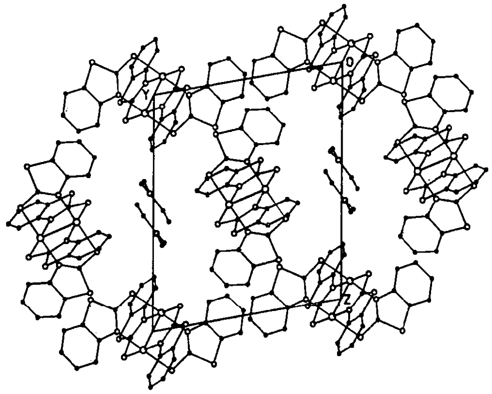

Fig. 2. *a*-Axis parallel projection, showing the cavities containing DMF molecules.

The mean Pt—Pt distance in the complex is shorter than the 2·775 Å reported for the parent metal (Donohue, 1974). Metal separation distances among dimeric, trimeric and tetrameric complexes of Pt^{II} appear to be a function of environment. In the tetragonal form of *cyclo*-tetrakis[di-μ-(acetato)-platinum(II)], in which the coordination about Pt^{II} is octahedral, the mean Pt—Pt distance is 2·495 Å (Carrondo & Skapski, 1978). In dimeric bis(dithiocumato)platinum(II) there is a Pt···Pt distance of 2·870 (2) Å in a distorted square antiprism of thiolato S atoms (Burke & Fackler, 1972). Trimeric bis(pyrazolato)platinum(II) contains a triangular distribution of Pt^{II} atoms bridged by three pairs of N,N pyrazolato anions in which the mean Pt···Pt separation distance is 3·048 Å (Burger & Strähle, 1985).

The Pt—S distances in $Pt_2(bztzt)_4$ [2·282 (2)–2·287 (2) Å] appear to correspond more closely to Pt—thiolate(S) than to Pt—thione(S) distances. Typical Pt—thiolate(S) distances occur in the range 2·281–2·333 Å (Burke & Fackler, 1972), whereas Pt—thione(S) distances mostly occur between 2·339 and 2·362 Å (O'Neill, Raper, Daniels & Nowell, 1982; Butler, Creighton, Raper & Tomlinson, 1986). The Pt—N distances [2·070 (4)–2·081 (1) Å] on the other hand are significantly longer than those reported for dimeric bis(pyrazolato)platinum(II) [1·997 (5)–2·027 (5) Å] (Burger & Strähle, 1985). Consequently, in comparison with related molecules the Pt—S distances in $Pt_2(bztzt)_4$ would seem to be relatively short and the Pt—N distances relatively long.

Deprotonation and coordination has generated some significant changes in bond lengths and angles in bztzt relative to the parent molecule, bztztH. These changes are concentrated in the S_{exo}—C—N and S_{exo}—C—S_{endo} region of the ligand; furthermore, there are some marginally significant differences in C—S_{exo} and C—N distances among the four crystallographically independent ligands (Table 2).

The mean C—S_{exo} and C—N distances in the ligands, 1·710 and 1·330 Å, are respectively longer and shorter than the corresponding distances, 1·662 (4) and 1·353 (6) Å, in bztztH (Chesick & Donohue, 1971; Radha, 1985). Consequently, the ligand is largely thiolate in character with only 42% π character in the C—S_{exo} bond compared to 61% in bztztH (Trinajstic, 1968).

The angles around the thiolato C atoms of the ligands also show some significant changes, relative to bztztH, with S_{exo}—C—N and N—C—S_{endo} increasing by about 2·5 and 4° respectively while the S_{exo}—C—S_{endo} and C—N—C angles decrease by about 7 and 3° respectively. These angular distortions may be seen to be a direct consequence of S,N coordination by the ligand.

Maximum deviations from the least-squares planes of the ligands occur with thione S [S(21), 0·0584 Å;

S(31), 0·0714 Å] and hetero N [N(1), −0·0336 Å; N(4), −0·0510 Å]. These displacements are also a consequence of S,N coordination by the ligand.

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Absolute Configuration and Structure of Carminic Acid* Existing as the Potassium Salt in *Dactylopius cacti* L.

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Abstract. $C_{22}H_{19}O_{13}^{-}.K^{+}.3H_2O$, $M_r = 584·53$, monoclinic, $P2_1$, $a = 8·867\,(2)$, $b = 7·126\,(1)$, $c = 19·207\,(3)$ Å, $\beta = 103·67\,(2)°$, $V = 1179·2\,(4)$ Å^3, $Z = 2$, $D_m = 1·621\,(1)$, $D_x = 1·646$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1·5418$ Å, $\mu = 26·99$ cm^{-1}, $F(000) = 608$, $T = 297$ K, $R = 0·042$ for 2196 independent reflections. Careful isolation of carminic acid has shown equimolar coexistence with potassium ions in *Dactylopius cacti* L., and the stereogeometry and the structural characteristics have been elucidated by X-ray analysis.

Introduction. Carminic acid is a natural anthraquinone dyestuff obtained from the insect *Dactylopius cacti* L. and is widely used as one of the most important red

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* Carminic acid is 7-*β*-D-glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracenecarboxylic acid (*Chemical Abstracts* name).

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